

# Electronic Supplementary Information for

## Catalytic Aerobic Oxidation of Renewable Furfural to Maleic Anhydride and Its Mechanistic Studies

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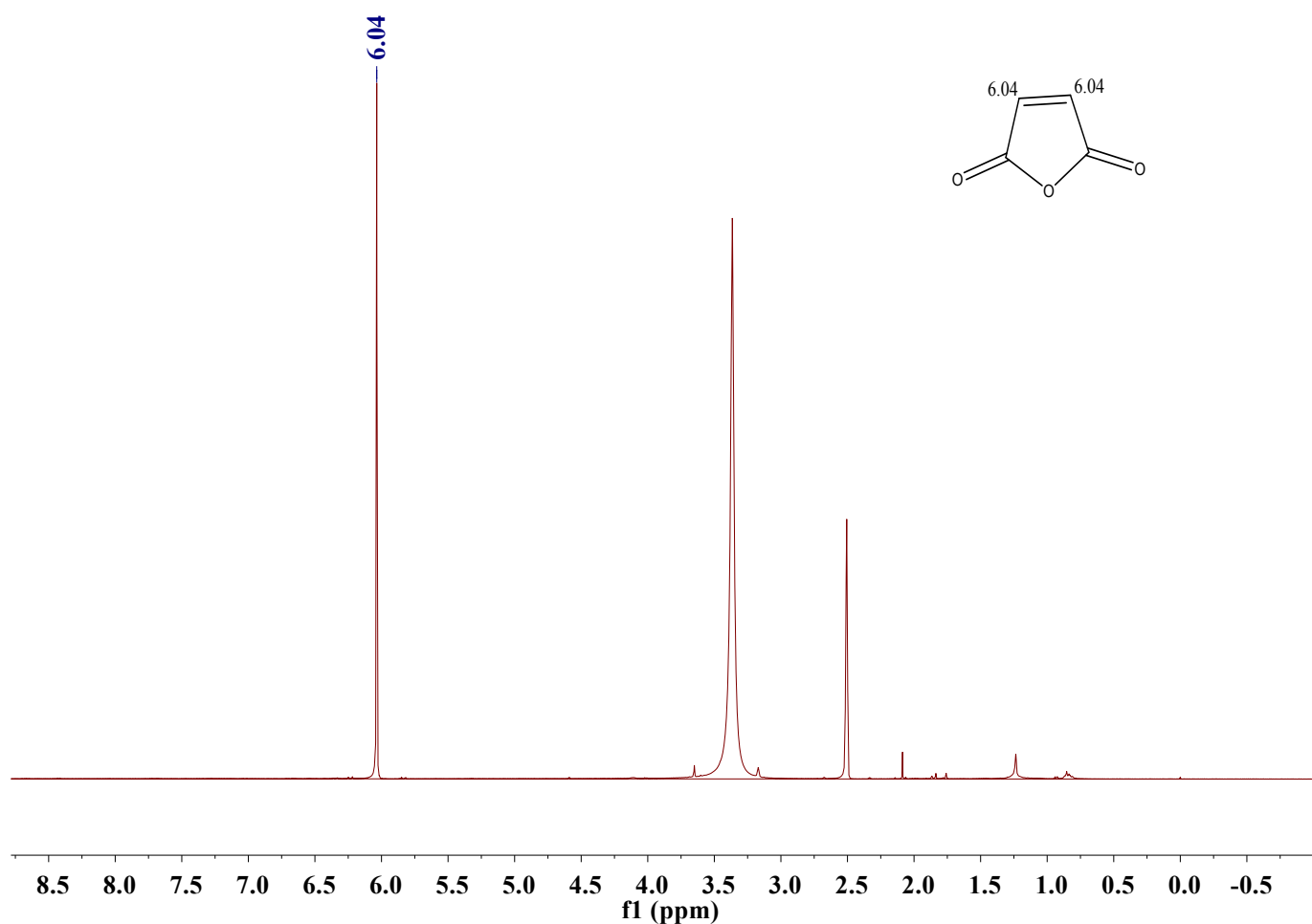
<sup>§</sup>These authors equally contribute to the work

### ***Content:***

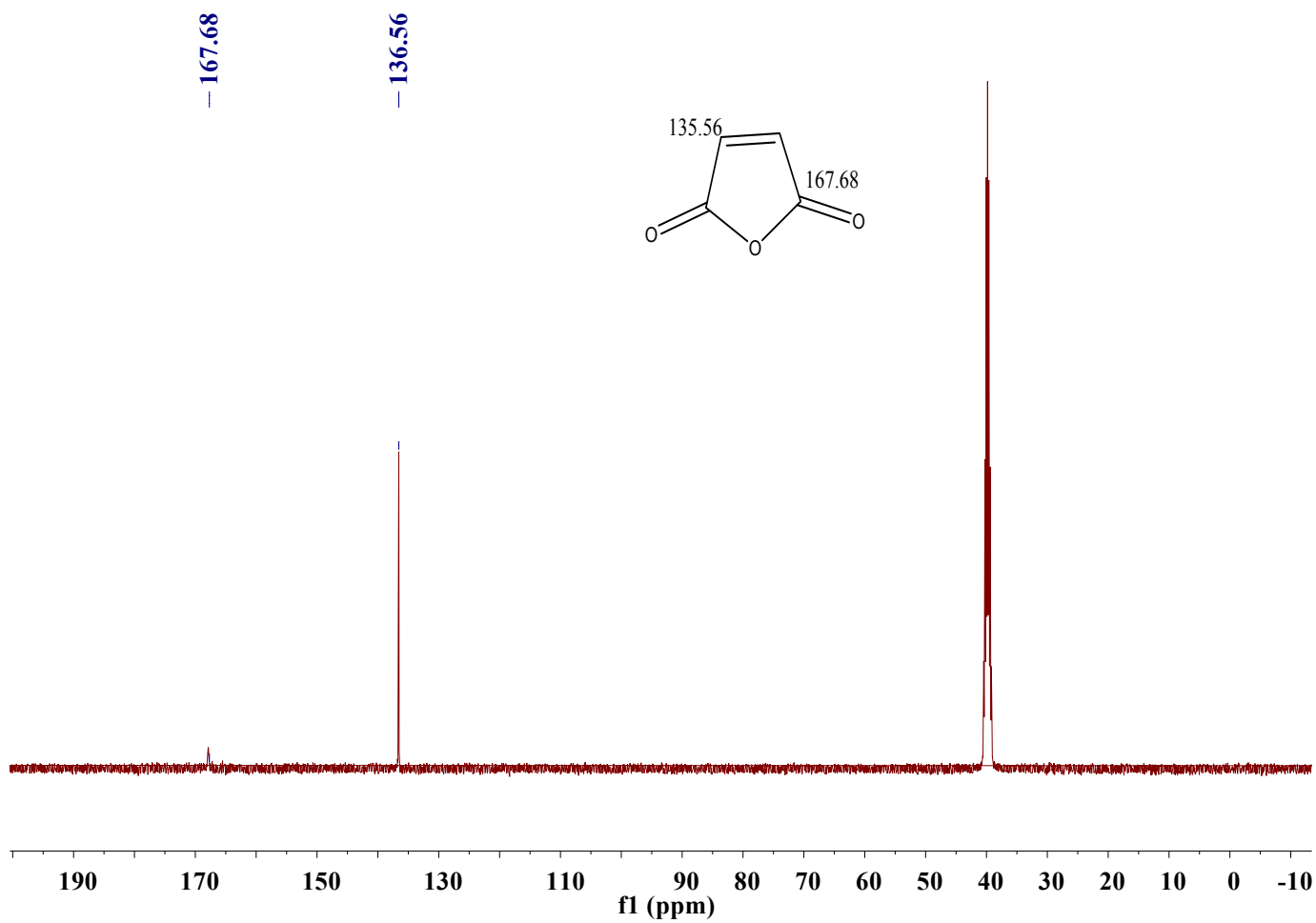
1. Isolation procedure of maleic anhydride product
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## 1. Isolation for maleic anhydride

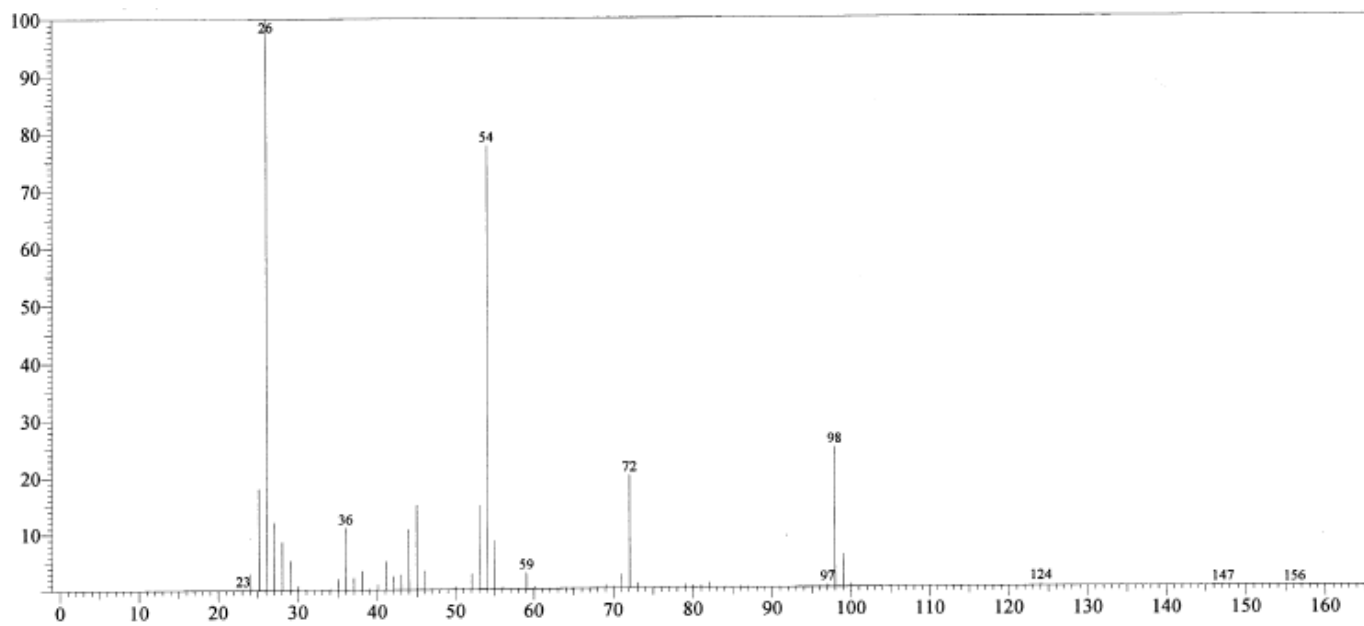
After 14 h reaction of normal furfural oxidation, the autoclave was cooled to room temperature, and depressurized to atmosphere pressure. After insoluble mass was filtered, acetonitrile and acetic acid in the clear solution were removed on rotary evaporator under vacuum. Then the resulting residue was further purified by silica gel chromatography with dichloromethane/methanol 30:1-0:1 as eluent, which provides 53.4% yield of maleic anhydride (1.27 mmol).



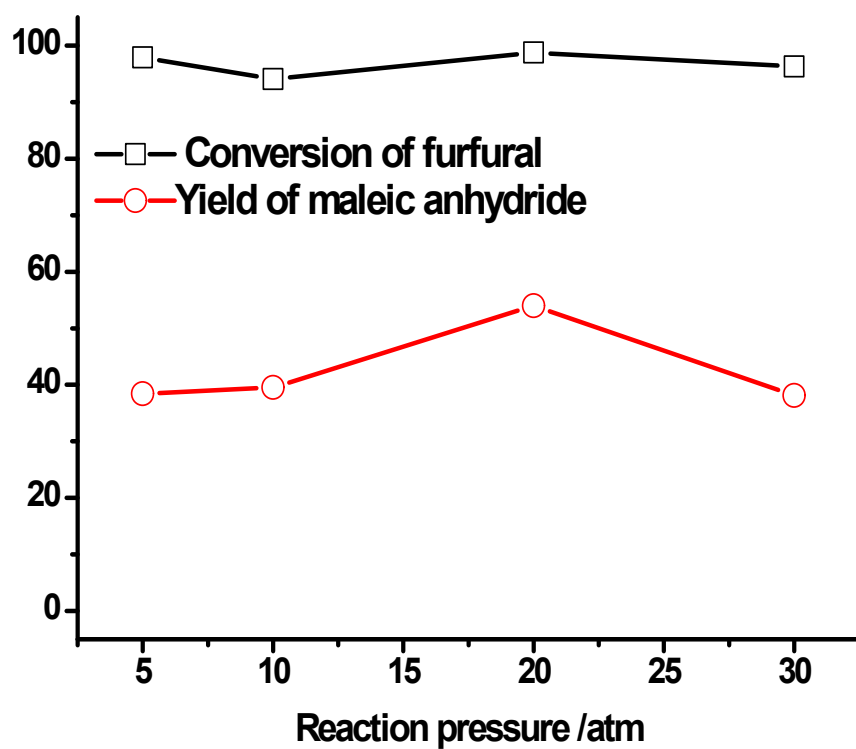
**Fig. S1** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) of isolated maleic anhydride in furfural oxidation (The signal at 2.5 is attributed to DMSO solvent residue, and the one at 3.3 is attributed to the water in DMSO-*d*<sub>6</sub>).



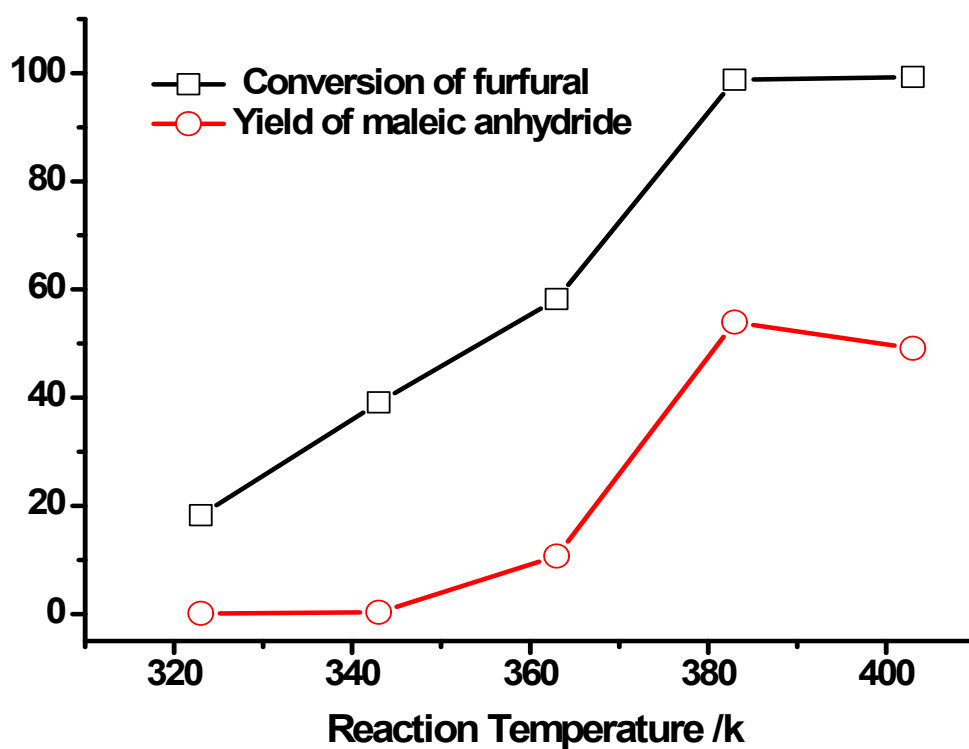
**Fig. S2**  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ) of isolated maleic anhydride in furfural oxidation.



**Fig. S3** MS(EI) spectrum of maleic anhydride in furfural oxidation.



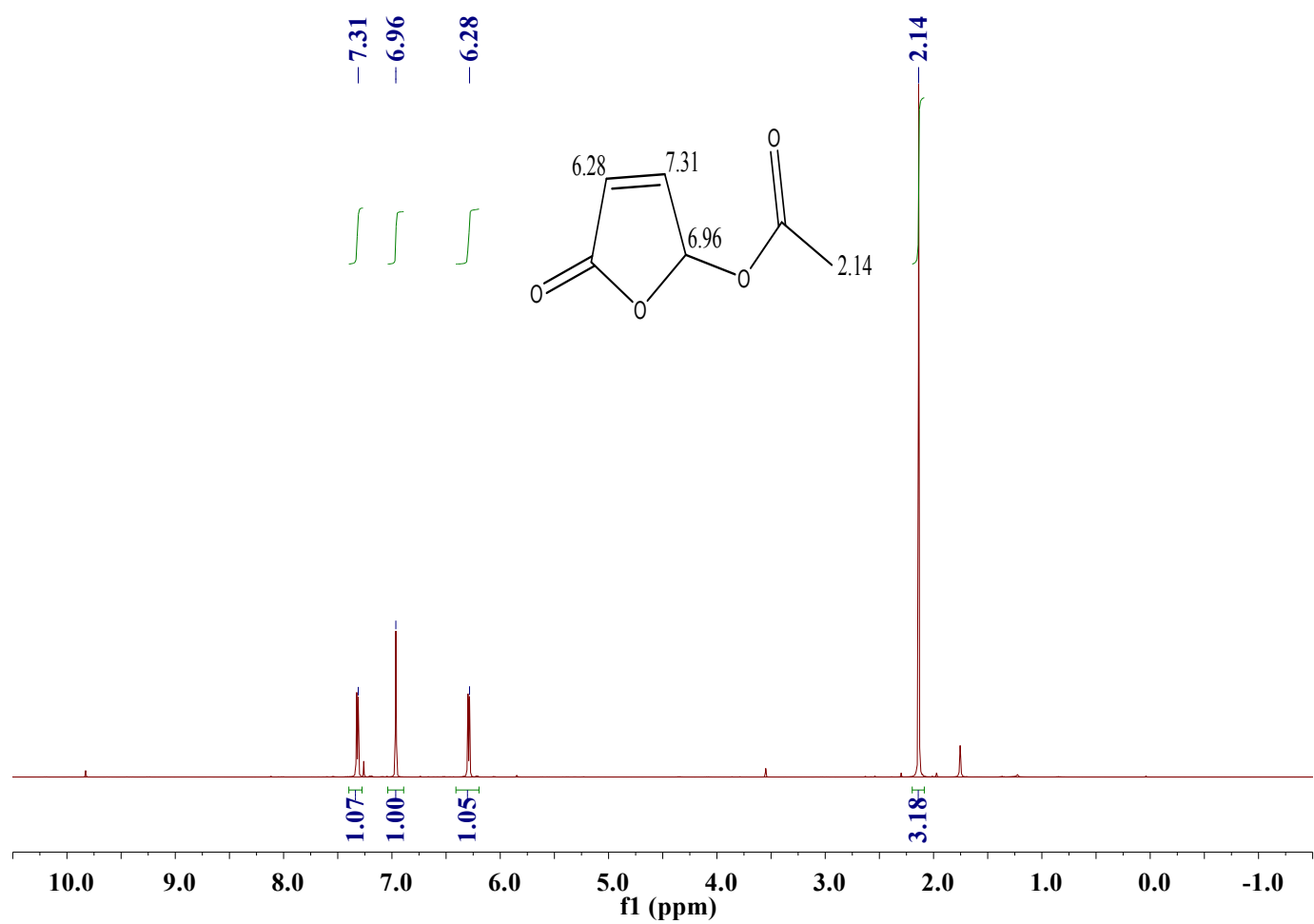
**Fig. S4** Effect of oxygen pressure on furfural oxidation. Conditions:  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$ , 0.02 mmol;  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ , 0.02 mmol; furfural, 2.4 mmol;  $\text{CH}_3\text{CN}$ , 2 mL; HOAc, 1.3 mL; temperature, 383 K; reaction time, 14 h.



**Fig. S5** Influence of the reaction temperature on furfural oxidation. Conditions:  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$ , 0.02 mmol;  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ , 0.02 mmol; furfural, 2.4 mmol;  $\text{CH}_3\text{CN}$ , 2 mL;  $\text{HOAc}$ , 1.3 mL;  $\text{O}_2$ , 20 atm; reaction time, 14 h.

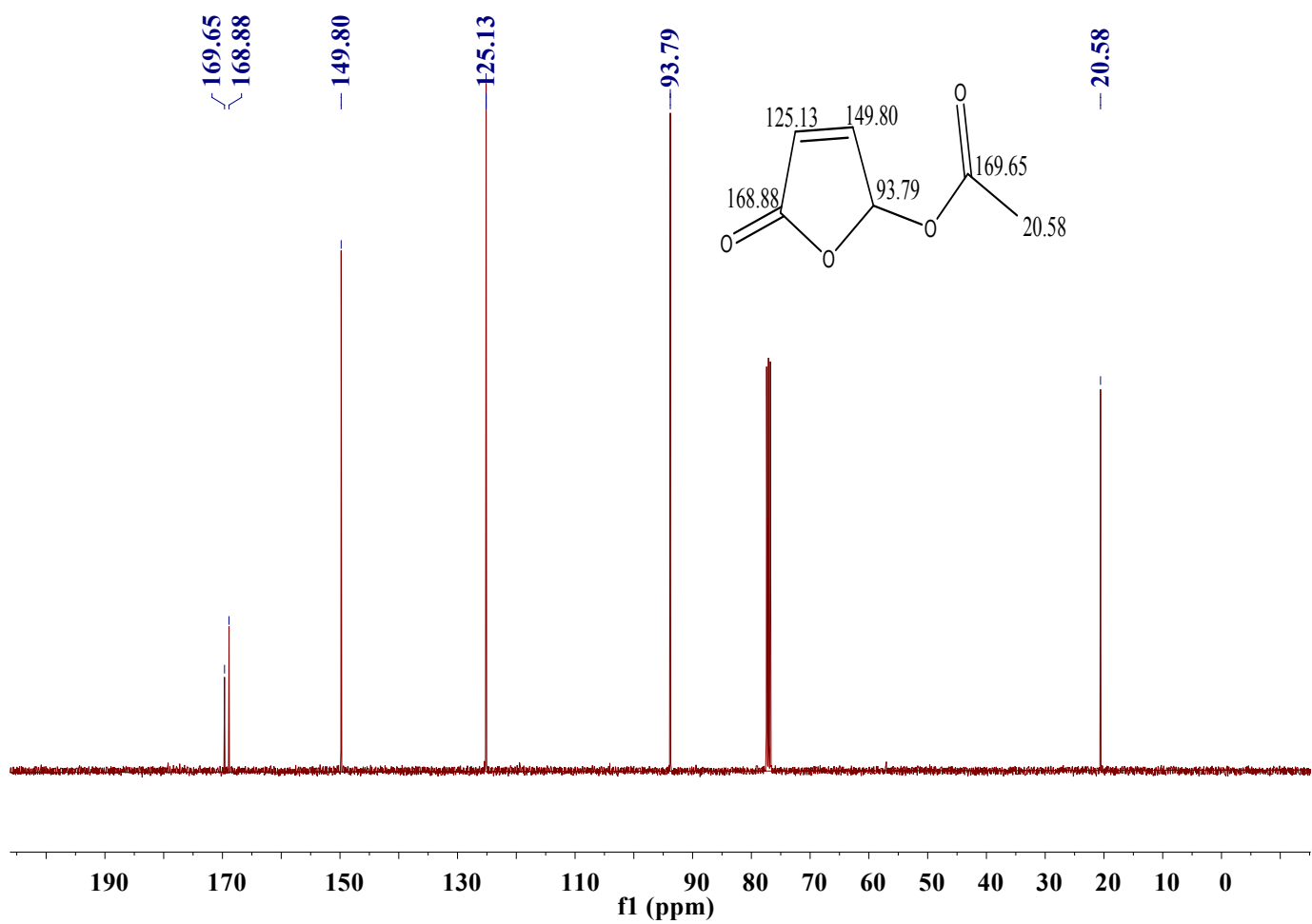
Table S1 Catalytic oxidation of furfural in different solvents						
Entry	solvent	Conversion	Yield	Yield	Yield	Total Yield <sup>[b]</sup>
		(%)	A(%)	B(%)	C(%)	(%)
1	2 mL CH <sub>3</sub> CN	97.9	32.0	/	0	32.0
2	2 mL HOAc	96.3	22.3	/	0.7	23.0
3	2 mL CH <sub>3</sub> CN + 0.1ml HOAc	99.4	37.2	/	0.7	37.9
4	2 mL CH <sub>3</sub> CN + 0.5 mL HOAc	91.4	36.6	/	2.3	38.9
5	2 mL CH <sub>3</sub> CN + 1.0 mL HOAc	99.6	37.8	/	7.0	44.8
6	2 mL CH <sub>3</sub> CN + 1.3 mL HOAc	98.7	54.0	/	7.5	61.5
7	2 mL CH <sub>3</sub> CN + 1.5 mL HOAc	95.7	41.9	/	8.5	50.4
8	2 mL CH <sub>3</sub> CN + 1.3 mL HOAc + 0.2ml Ac <sub>2</sub> O	99.3	37.7	/	11.4	49.1

[a] Condition: 0.02 mmol H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>·xH<sub>2</sub>O, 0.02 mmol Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, 2.4 mmol furfural, 20 atm O<sub>2</sub>, 383 K, 14 h. [b] Total yield of maleic acid, maleic anhydride and 5-acetoxy-2(5H)furanone.



**Fig. S6** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of isolated 5-acetoxy-2(5H)furanone in furfural oxidation.



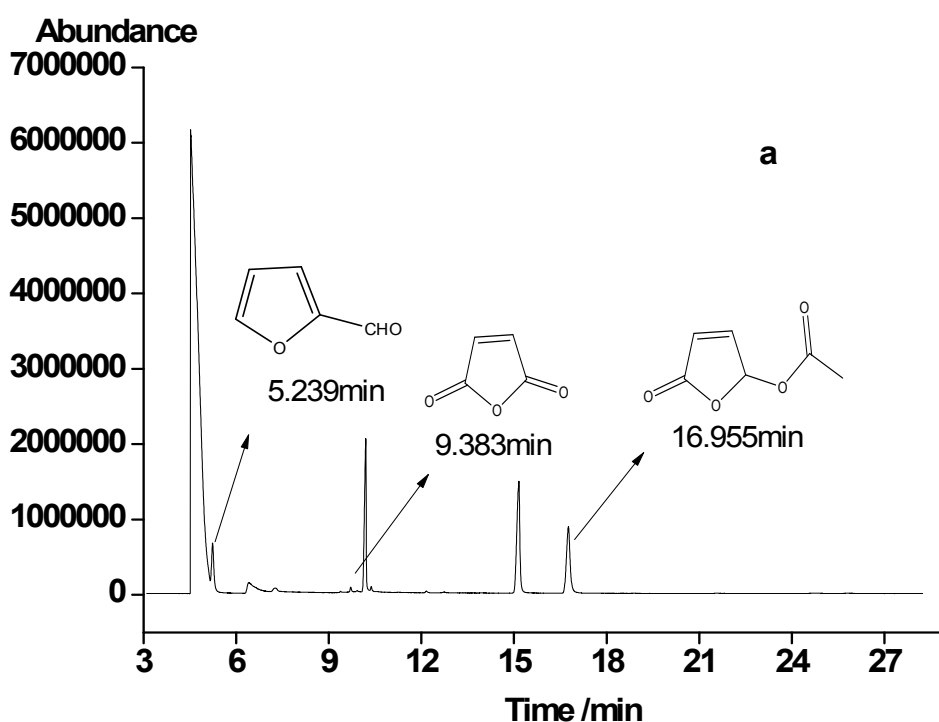


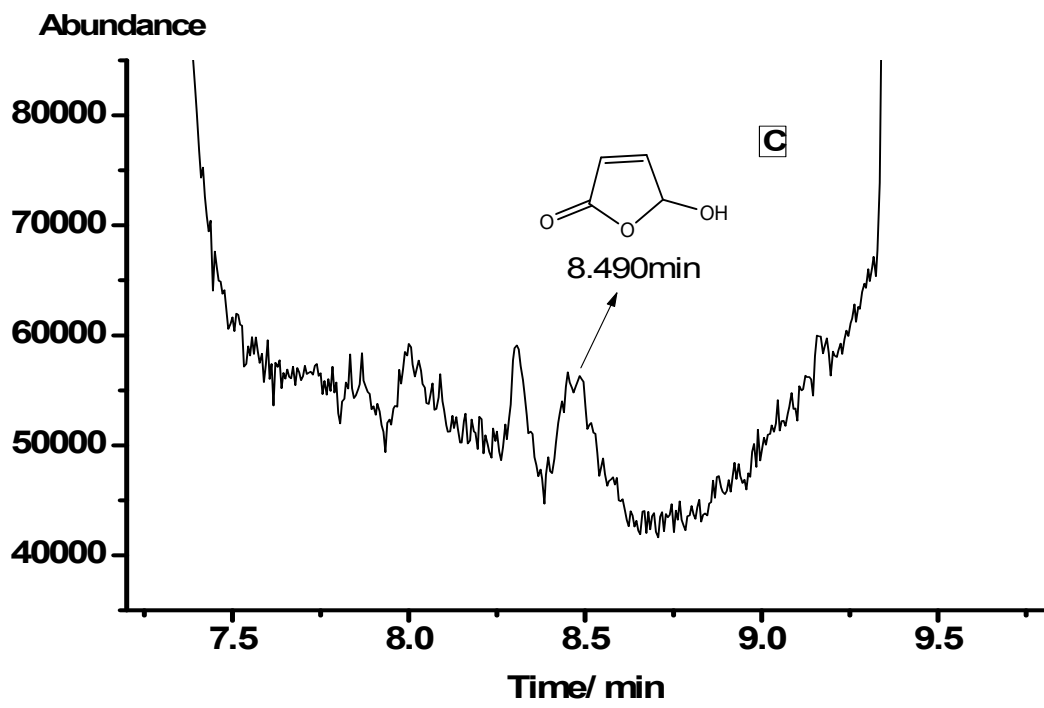
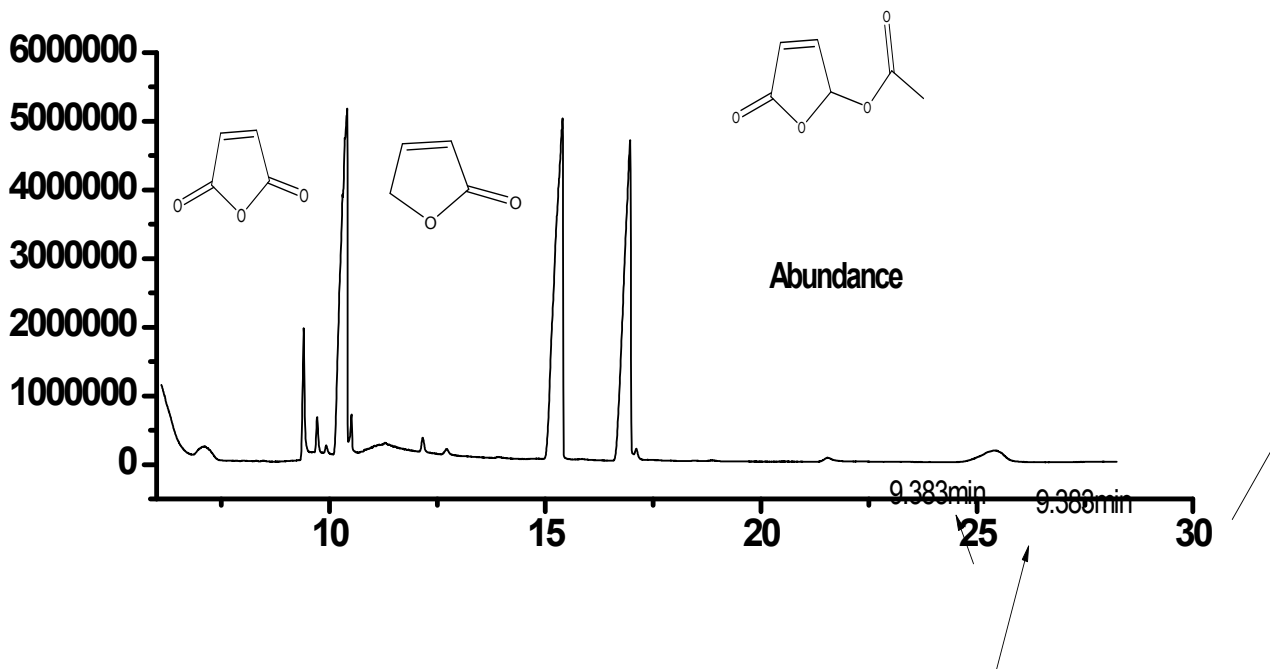
**Fig. S7**  $^{13}\text{C}$  NMR spectrum (400MHz,  $\text{CDCl}_3$ ) of isolated 5-acetoxy-2(5H)furanone in furfural oxidation.

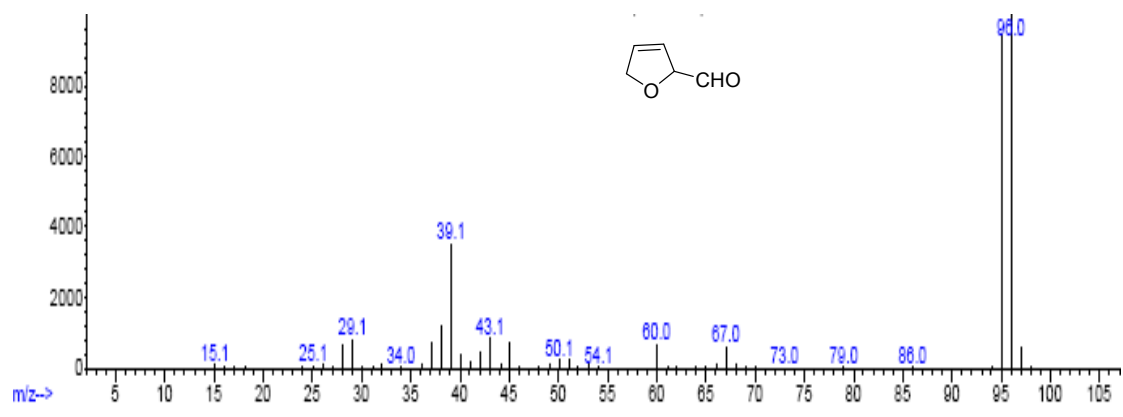
## GC-MS data for catalytic furfural oxidation by $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$ and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$

GC-MS was employed to identify the intermediates and products in furfural oxidation. Conditions : furfural, 2.4 mmol;  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$ , 0.02 mmol;  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ , 0.02 mmol;  $\text{CH}_3\text{CN}$ , 2 mL;  $\text{HOAc}$ , 1.3 mL;  $\text{O}_2$ , 20 atm; temperature, 383 K; reaction time, 14 h.

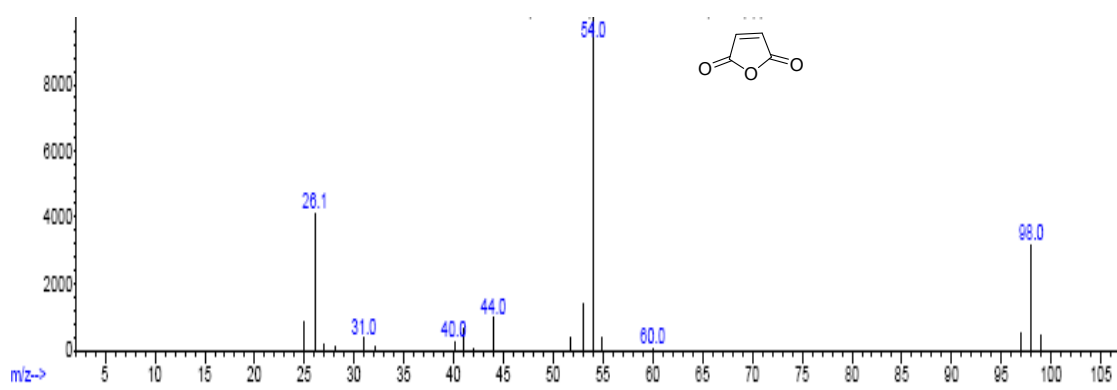
The measurements were conducted with auto sampler, DB-Wax capillary column and a flame ionization detector. Figure a demonstrates the GC-MS graph with a normal dosage of sample, Figure b displays the GC-MS graph with a higher dosage of sample to track the potentially trace intermediates, and figure c is the amplification section of the retention time from 7.2 min to 9.7 min in Figure b.



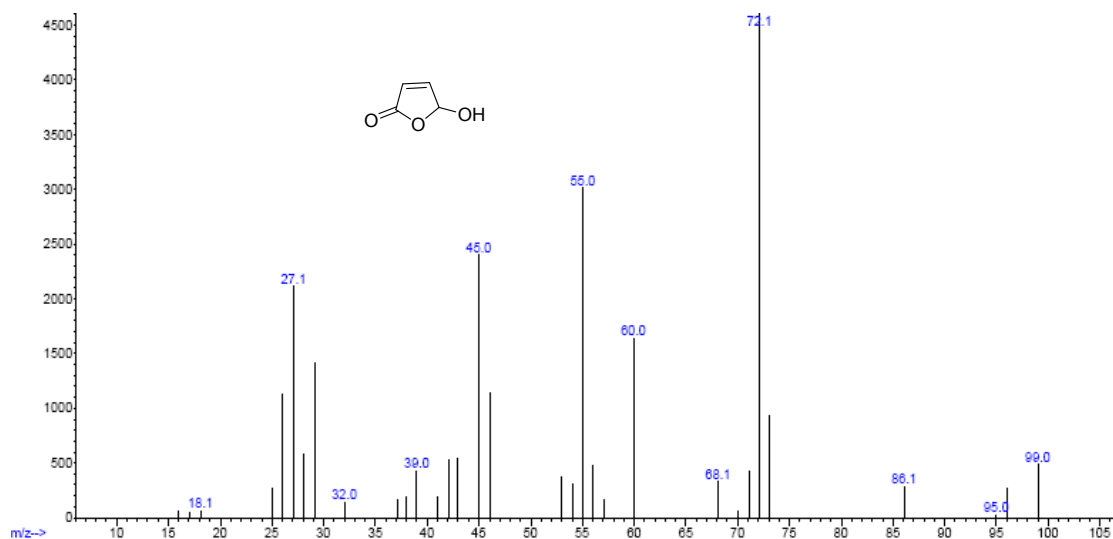




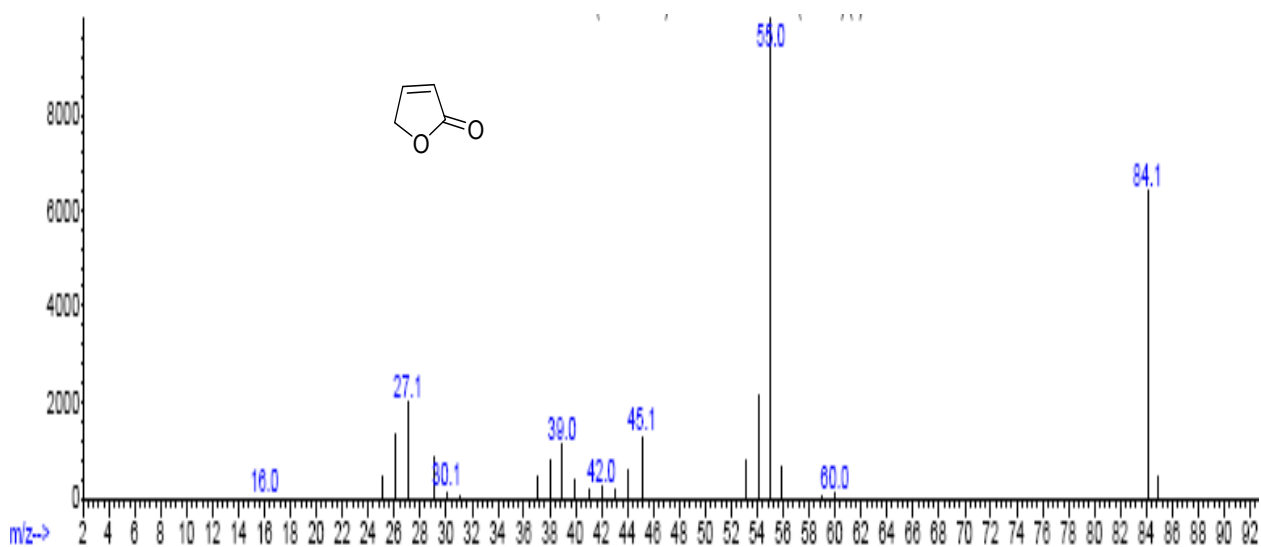
**Fig. S8-1** MS graph of furfural from catalytic furfural oxidation by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$  plus  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ .



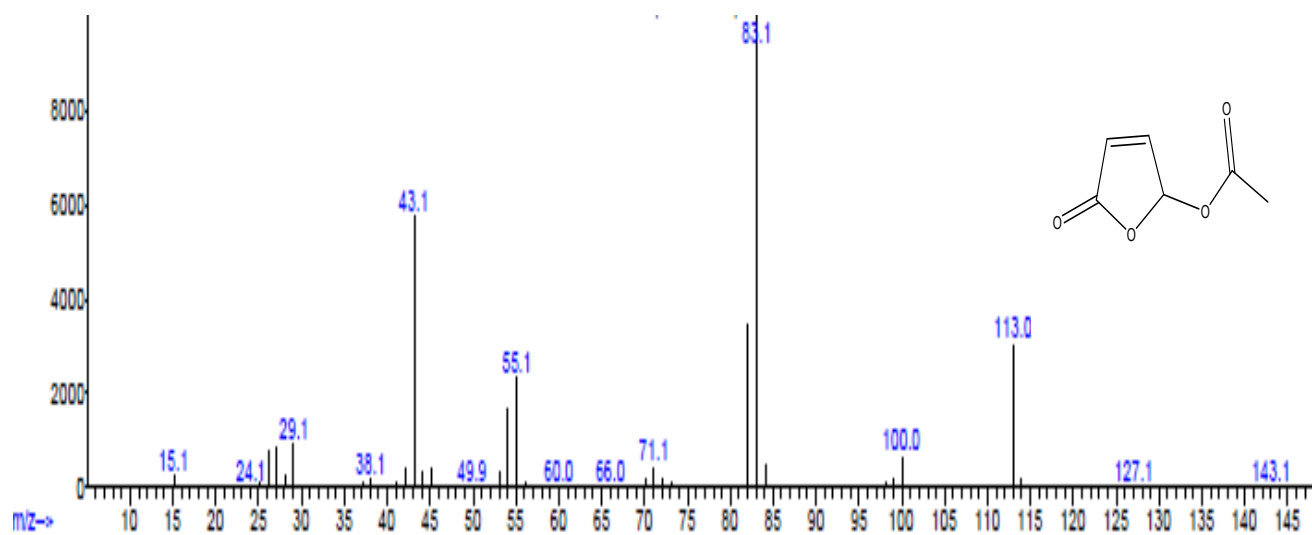
**Fig. S8-2** MS graph of maleic anhydride from catalytic furfural oxidation by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$  plus  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ .



**Fig. S8-3** MS graph of 5-hydroxy-2(5H)-furanone from catalytic furfural oxidation by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot x\text{H}_2\text{O}$  plus  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ .



**Fig. S8-4** MS graph of 2(5H)-furanone from catalytic furfural oxidation by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \cdot x\text{H}_2\text{O}$  plus  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ .



**Fig. S8-5** MS graph of 5-acetoxy-2(5H)-furanone from catalytic furfural oxidation by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}\cdot x\text{H}_2\text{O}$  plus  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ .